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Abstract

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ON ALKYL ESTERS OF ETHYLTHIOARSINOUS ACID

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Esters of thioarsenous, alkyl- and arylthioarsinous acids have been little studied (^{1}). In the patent literature (^{2}), some esters of arylthioarsinous acids are described as substances possessing therapeutic activity.

In the present work, the synthesis and properties of alkyl esters of ethylthioarsinous acid of the general form $C_2H_5As(SR)_2$ are described.

In our investigations we focused above all on the study of the reaction of direct interaction of ethyldichloroarsine with the corresponding mercaptans according to the scheme:

$$C_2H_5AsCl_2 + 2RSH \rightarrow C_2H_5As(SR)_2 + 2HCl.$$

Experiments by the first method were carried out as follows. The required amount of mercaptan was placed in an Arbuzov distillation flask, and ethyldichloroarsine was added to it dropwise from a dropping funnel. Hydrogen chloride was vigorously evolved; it was displaced by a stream of dry carbon dioxide. After the addition of ethyldichloroarsine was completed, the mixture was slowly heated first to the boiling temperature of the mercaptan and then gradually to a temperature of 190–200° over the course of 3 hours. The reaction products were then distilled in vacuum. In this way we synthesized the ethyl, *n*-propyl, *n*-butyl, and isoamyl esters of ethylthioarsinous acid.

By the second method, i.e., by the interaction of ethyldichloroarsine and the corresponding mercaptan in ether and in the presence of anhydrous pyridine, we obtained the ethyl, *n*-butyl, and *n*-hexyl esters of ethylthioarsinous acid.

It should be noted here that purer preparations are obtained if, after separation of the main mass of pyridine hydrochloride, the filtrate is quickly washed with ice water.

The ethyl ester of ethylthioarsinous acid was also obtained by a third method according to the scheme:

$$2C_2H_5SNa + C_2H_5AsCl_2 \rightarrow C_2H_5As(SC_2H_5)_2 + 2NaCl.$$

The constants of the thioesters isolated by us are presented in Table 1. The alkyl esters of ethylthioarsinous acid synthesized by us are colorless, transparent liquids with an unpleasant persistent odor, readily soluble in many organic solvents.

Hydrolysis of alkyl esters of ethylthioarsinous acid in the cold and at ordinary temperature proceeds comparatively slowly; on standing in air, a white precipitate forms. On heating the *n*-butyl ester of ethylthioarsinous acid with water, we isolated ethylarsinous acid.

Its formation can readily be explained by the following reactions:

$$C_2H_5As(SC_4H_9)_2 + 2HOH \rightarrow C_2H_5As(OH)_2 + 2C_4H_9SH \quad (1)$$

$$C_2H_5As(OH)_2 + O_2 \rightarrow 2\,C_2H_5AsO(OH)_2 \quad (2)$$

Equation (1) is identical with the equation for the hydrolysis reaction given by Voter and Williams (^{3}) for analogous compounds.

Table 1

Formula	Method of preparation	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D found	R_D of arsenic	As, % found	As, % calc.	S, % found	S, % calc.	Yield, %
$C_2H_5As(SC_2H_5)_2$	I	80–82/2	1.2555	1.5750	59.54	10.412	33.51	33.11	28.65	28.35	30.4
$C_2H_5As(SC_2H_5)_2$	II	81–82/2	1.2593	1.5747	59.34	10.21	32.93	33.11	28.65	28.35	35.5
$C_2H_5As(SC_2H_5)_2$	III	75–77/1.5	–	1.5749	–	–	33.28	33.11	28.9	28.35	41.9
$C_2H_5As(SC_3H_7)_2$	I	101–102/2	1.1906	1.5565	68.70	10.34	29.38	29.45	25.58	25.22	40.3
$C_2H_5As(SC_4H_9)_2$	I	122–123/2	1.1402	1.5442	78.19	10.69	26.61	26.53	23.26	22.71	54.7
$C_2H_5As(SC_4H_9)_2$	II	122–123/2	1.1374	1.5441	78.37	10.97	26.12	26.53	22.96	22.71	59.4
$C_2H_5As(SC_4H_9)_2$	III	120–123/2	1.1396	1.5442	78.23	10.63	26.38	26.53	22.51	22.71	43.5

Formula	Method of preparation	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D found	R_D of arsenic	As, % found	As, % calc.	S, % found	S, % calc.	Yield, %
$C_2H_5As(SC_5H_{11})_2$-*n*		135–136/2	1.0957	1.5324	87.83	10.99	24.07	24.14	20.99	20.66	43.2
$C_2H_5As(SC_6H_{13})_2$	I	163–164/1.5	1.0778	1.5280	96.62	10.55	21.84	22.13	18.78	18.95	31.3
$C_2H_5As(SC_6H_{13})_2$	II										

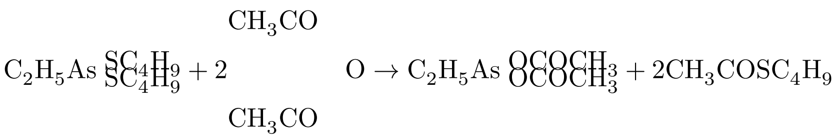
Next we studied the reaction of the interaction of the *n*-butyl ester of ethylthioarsinous acid with methyl iodide. After a 13-day standing of a mixture of equimolecular amounts of methyl iodide and the *n*-butyl ester of ethylthioarsinous acid at a temperature of 20–22°, white crystals separated. Their m.p. was 78–80°. They dissolved well in water and alcohol and did not dissolve in ether. According to the analytical data, this substance is dimethyl-*n*-butylsulfonium iodide. The formation of the latter can be explained by the following scheme:

$$C_2H_5As(SC_4H_9)_2 + 4CH_3J \rightarrow 2\left[(C_4H_9S(CH_3)_2)\right]J^- + C_2H_5AsJ$$

Thus, it has been shown that, under the action of methyl iodide, alkyl esters of ethylthioarsinous acid do not form compounds of the arsonium type, and, owing to the presence of more reactive centers at the sulfur atoms, the As—S bond is destroyed with the formation of sulfonium compounds.

We also studied the reactions of the interaction of the *n*-butyl ester of ethylthioarsinous acid with acetic acid chloride and acetic anhydride. In both cases a double-exchange reaction takes place, analogous to the previously studied reactions of the interaction of acid chlorides and anhydrides of carboxylic acids with esters of arsenous and alkylarsinous acids (^{4}), according to the following schemes:

$$C_2H_5As\begin{smallmatrix}SC_4H_9\\SC_4H_9\end{smallmatrix} + 2CH_3COCl \rightarrow C_2H_5AsCl_2 + 2CH_3COSC_4H_9$$



$$C_2H_5As\begin{smallmatrix}SC_4H_9\\SC_4H_9\end{smallmatrix} + 2\begin{matrix}CH_3CO\\ \\ CH_3CO\end{matrix}O \rightarrow C_2H_5As\begin{smallmatrix}OCOCH_3\\OCOCH_3\end{smallmatrix} + 2CH_3COSC_4H_9$$

Both reactions require prolonged heating for 5 to 18 hours at a temperature of 150–160°. The S-butyl ester of thioacetic acid isolated by us in these reactions is a colorless transparent liquid with a sharp odor, partly reminiscent of the odor of butyl acetate. The ester is readily soluble in organic solvents and is immiscible with water. B.p. 89°/74 mm, d_4^{20} 0.9441; n_D^{20} 1.4598.

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